SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYAMIDES AND BLOCK COPOLYESTERS

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ABSTRACT

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The syntheses and characterization of block copolyamides and block copolyesters are discussed. Poly(1,2-cyclohexalene-trans-1,4-cyclohexane dicarboxamide : 1,4-phenylene terephthalamide); poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate : 1,4-phenylene terephthalate); poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate : 2-methyl-(1,3-phenylene terephthalate); poly(trans-1,2-cyclohexalene-trans-1,2-cyclohexanedioate : 2-methyl-1,3-phenylene isophthalate); and poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate) were prepared. Attempts made to prepare poly(1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxamide : 1,4-phenylene, 4-methyl phthalamide) and poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate : 1,4-phenylene terephthalate) were unsuccessful. The syntheses of the above block copolymers, in each case, required coupling an aliphatic prepolymer with an aromatic prepolymer. These were achieved by using two methods - first, by condensing a polymer having hydroxyl end groups with another having acid chloride end groups, and

second, by coupling, two prepolymers having terminal hydroxyl groups with an acid chloride. The characterization of these block copolymers and the corresponding prepolymers was accomplished using spectroscopic techniques (infrared and proton and carbon-13 nuclear magnetic resonances) solution viscosity, differential scanning calorimetry, and elemental analysis.

DEDICATION

To the memory of my father, Rev. Canon Isaiah Iwuanyanwu Akubuiro, and to my mother, Mrs. Catherine A. Akubuiro for her patience, support, thoughtfulness, and also for her endurance of the inconveniences associated with my absence from home.

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INTRODUCTION

Significant advances have been made in the synthesis, characterization, and utilization of block copolymers in the past seventeen years and although a complete knowledge is not yet available, we have enough evidence now about the range of properties displayed by block copolymers in which two or more polymeric segments are attached end-to-end by covalent bonds.[1-5]

When polymers are composed of chemically and sterochemically identical units (with exclusion of terminal groups), they are called homopolymers, while a polymeric chain comprising more than one type of repeating unit is termed a copolymer. When a polymer (except a homopolymer) is used to produce a block copolymer, the polymer is called a prepolymer. There are four types of copolymers:[1-6] alternating, block or ordered, graft and random copolymers. The alternating copolymers have one unit followed by another unit of a different kind, for example:

-XYXYXYXYXY-

where X and Y represent the structural or repeating unit. Block or ordered copolymers are polymeric compounds consisting of chemically dissimilar, long sequences of homopolymer or prepolymers which are terminally connected. An example is:

-XXXXXXXYYYYYYYXXXXXXXYYYYYYY-

This could be represented as $-(A-B)_n-$, where A and B represent polymeric segments. Graft copolymers are chemically connected homopolymers or prepolymers, which are similar to block copolymers in many ways, for example:

```
-X X X X X X X X X X X X X X-
      Y       Y       Y
      Y       Y       Y
      Y       Y       Y
      1       1       1
```

Due to the similarity in some of the synthetic techniques employed for the two types of copolymers, block copolymers have been considered as a limiting case of graft copolymers.[1] Finally random copolymers,[5] unlike alternating copolymers, are characterized by a statistical assignment of the comonomer repeat units along the backbone of the chain, for example:

-XXYYYXYXXYYX-

In the context of our definition of alternating copolymers, one might be tempted to classify some of the known homopolymers as perfectly alternating copolymers. Nonetheless, since they are characterized by the presence of an exact repeat of the structural unit, they are preferably classified as homopolymers.

Since we defined block copolymers as a sequential arrangement of polymer segments terminally connected by covalent bonds, we will expect them to display various segmental architectures ranging from A-B structures, containing two

segments only, to A-B-A block copolymers with three segments, to multiblock -(A-B)$_n$- systems composed of many segments.

Sophisticated experimental techniques have to be used in the preparation of the above, well-defined structures.[5] These include (a) accurate knowledge and control of initiating and propagating species, (b) minimum level of impurities, (c) the use of low-concentration solution polymerization methods, and/or (d) the need for separately producing reacting polymeric intermediates of known functionality.

There are two methods[7] by which formation of block copolymers and other macromolecules can be achieved. These are addition and condensation polymerizations. In addition polymerization monomeric compounds containing reactive double bonds or reactive ring structures are changed into macromolecules by continued addition of monomer units either spontaneously or under the influence of initiators or catalysts. The mechanism of the addition polymerization may be either radical, cationic, or anionic. In condensation polymerization, also known as polycondensation or step-growth polymerization, polymers are produced through the chemical linkage of two bifunctional or polyfunctional molecules, with the elimination of a low-molecular weight by-product (e.g., water, alcohol, hydrogen chloride). There is also a class of polymers which are classified as condensation polymers. The formation of this class of polymers does not proceed by a true condensation reaction but rather involves an addition process whereby a hydrogen is transferred. An example of this is the addition of a diol to a diisocyanate to form a polyurethane. Unlike the chain-growth process[2] (e.g., free radical polymerization reactions) in which a rapid growth of the individual polymer chain takes place and where the initiation, propagation, and termination reactions have different mechanisms and rate, the step-growth process is characterized by a relatively slow

and stepwise addition of a monomer to a polymer chain with essential identity in mechanism and rate of the initiation, propagation, and termination reactions.

Regardless of the differences between addition and step-growth processes, they allow the control of block integrity and fulfillment of the architectural (sequential) requirement essential for desirable properties.[5] The synthetic technique applicable to A-B and A-B-A architectures is the anionic living polymerization, and that for $-(A-B)_n-$ structure is most often the step-growth process. Due to the statistical nature of the stoichiometrically controlled reactions of the step-growth polymerization, it is difficult to prepare the A-B and A-B-A structures via this process. On the other hand, due to the high probability of early chain termination caused by the presence of impurities, it is impossible to form well-defined $-(A-B)_n-$ structures through a living addition process.

With sequential anionic addition polymerization, synthesis of block copolymers that have predictable molecular weights and narrow molecular weight distributions can be accomplished. A long block length can also be obtained since the block molecular weight is governed by monomer to initiator ratio. Although the above is not readily accomplished with the step-growth process, this process has the advantage of being able to offer a wider spectrum of chemical structures which include many high performance substances.

We employed the step-growth process to prepare the block copolyamide and block copolyester ($-(A-B)_n-$) structures of interest. The individual components incorporated in the block were prepared separately with known functional terminal groups. We were interested in preparing block copolymers in which an aliphatic ring structure is combined in block with an aromatic ring structure. We expected

these block copolymers to possess very interesting thermal and mechanical properties. A tough elastomer should be produced, for example, by combining the flexible cyclohexane rings in blocks with the relatively rigid phenyl rings. The resulting block copolymer should have thermal transitions that are characteristic of the individual sequences incorporated in the block. Generally,[2,5,7] the properties of block copolymers are additive properties of the corresponding homopolymers so that it is possible to synthesize block copolymers that possess the desired combination of properties. However, this cannot be obtained by merely blending the respective homopolymers since chemically different polymers are seldom compatible with one another.

EXPERIMENTAL

Viscosity Measurements

The inherent viscosity numbers $\eta_{inh} = 2.3 \log (\eta_{rel})/C$ were determined at 30° for solutions containing 0.5 g of polymer per 100 ml of solvent with a Cannon-Fenske viscometer. Results are reported in deciliters per gram, dl/g.

Spectroscopic Techniques

For the infrared spectra, the Beckman 4240 infrared spectrophotometer was used; where this is not so, specifications are made. The Bruker 250 MHz spectrometer was employed for running the carbon-13 and the proton nuclear magnetic resonance spectra.

Calorimetric Techniques

Glass transition (T_g) and melting (T_m) temperatures were determined by using the DuPont 990 and 1090 Thermal Analyzers with the DuPont 910 Differential Scanning Calorimeter.

Purification of Materials

Solvents: The solvents used were reagent or spectrograde chemicals. The o-dichlorobenzene used in the polyesterification process was purified and dried by fractional distillation over calcium hydride, b.p. 180°. The N,N-dimethylacetamide (DMAc) was purified by fractional distillation over calcium hydride and dried by storage over Davidson's molecular sieve.

Intermediates: The diols and diamines were purchased from Aldrich Chemical Company unless otherwise specified. The acid chlorides (with exception of terephthaloyl chloride and isophthaloyl chloride which were purchased from Aldrich) were synthesized. These intermediates were purified either by solvent crystallization or vacuum distillation as deemed necessary. The terephthaloyl chloride was recrystallized from dry hexane (dried by storage over calcium chloride). This was accomplished by using 100 g of terephthaloyl chloride per 700 ml of hexane, m.p. 81-82°. The 1,4-phenylenediamine was recrystallized using an acetone-chloroform mixture (1/1), m.p. 140°. The 1,4-phenylenediamine and terephthaloyl chloride were dried in a vacuum oven at room temperature. For the terephthaloyl chloride and all other acid chlorides, minimum exposure to moisture was maintained since they are susceptible to hydrolysis. The 1,2-diaminocyclohexane (Pfaltz and Bauer) was fractionally distilled, b.p. 185°. Hydroquinone was purified by recrystallizing four times from water which had been deoxygenated by boiling and cooled with a stream of bubbling nitrogen.

Preparation of the Acid Chlorides

trans-1,4-Cyclohexane dicarboxylic acid chloride: This acid chloride was prepared by reacting 25 g of trans-hexahydroterephthalic acid (Aldrich) with 65 g of phosphorus pentachloride in anhydrous ether medium (dried by storing over calcium hydride overnight). The solution was refluxed for 5 hr after which it was allowed to cool. After the unreacted acid had been filtered off, the acid chloride solution was subjected to vacuum distillation. The ether was distilled off at 15° and phosphorus

oxychloride ($POCl_3$) at 35° (ca. 10 mmHg). After complete evacuation of the ether, water, and $POCl_3$, distillation was stopped. Crystals formed after the solution was allowed to cool. The trans-hexahydroterephthaloyl chloride crystals were collected and washed with dry hexane, m.p. 69-71°. These was dried in a vacuum oven at room temperature for 24 hr.

trans-1,2-Cyclohexanedicarboxylic acid chloride: Into a 500 ml round bottom flask equipped with a magnetic stirrer, condenser, and drying tube, and containing 200 ml of dry anhydrous ether was added 20 g of trans-1,2-cyclohexanedicarboxylic acid (Pfaltz and Bauer). To this stirred solution was added 56 g of phosphorus pentachloride (PCl_5). The mixture was refluxed for 4 hr. At 5 mmHg, the ether was distilled off at 12° and water at 25°. The $POCl_3$ was distilled off at 51° (60 mmHg). The trans-hexahydrophthalic acid chloride was collected between 168° and 175° (ca. 120 mmHg). The amount of acid chloride collected was 16.3 g. This represents a 71% yield.

cis-1,2-Cyclohexanedicarboxylic acid chloride: Into a 250 ml round bottom flask equipped with a magnetic stirrer, condenser, and drying tube was added 20 g of cis-1,2-cyclohexanedicarboxylic acid anhydride (Aldrich). To this was added 34 g of phosphorus pentachloride. The mixture was heated gently until melting took place, and was then brought to reflux and allowed to reflux for 5½ hr. The phosphorus oxychloride ($POCl_3$) was distilled off between 28 and 33° (10 mmHg). The amount of $POCl_3$ distilled off was 14 ml. The receiver and condenser were changed after the $POCl_3$ had been thoroughly evacuated. The cis-hexahydrophthalic acid chloride was collected at 105° (ca. 10 mmHg); 23.7 g was collected. This was an 87.4% yield.

These acid chlorides were used as soon as possible or stored under nitrogen in dry boxes because they are highly susceptible to hydrolysis. Triethylamine was distilled over calcium oxide, and lithium chloride (LiCl) was dried overnight in an oven. The prepurified nitrogen used was passed through anhydrous $CaSO_4$ (Drierite).

Preparation of Polymers

Poly(1,2-cyclohexalene-trans-1,4-cyclohexane dicarboxamide : 1,4-phenylene terephthalamide)

Poly(1,2-cyclohexanelene-trans-1,4-cyclohexanedicarboxamide:1,4-phenylene terephthalamide) was prepared by reacting a low molecular weight poly(1,4-phenylene terephthalamide) having acid chloride end groups with a low molecular weight poly(1,2-cyclohexane-trans-1,2-cyclohexane dicarboxamide) having terminal amino groups.

Poly(1,4-phenylene terephthalamide): A 250 ml three-necked, round bottom flask equipped with a magnetic stirrer was charged with 2.162 g (0.02 mole) of para-phenylenediamine, 5.64 ml of triethylamine, 1.92 g of lithium chloride (LiCl), and 35 ml of N,N-dimethylacetamide. To this was added, 4.468 g (0.022 mole) of terephthaloyl chloride dissolved in 15 ml of N,N-dimethylacetamide. An additional 5 ml was used to rinse the residue from the dropping funnel. The above amount of acid chloride represents a 10 mole percent excess of the equivalent amount of the diamine. The lithium chloride was 3.2 weight percent in solvent.

Poly(1,2-cyclohexalene-trans-hexahydroterephthalamide): A low molecular weight poly(1,2-cyclohexalene-trans-hexahydroterephthalamide) with amino end groups

was prepared in a similar fashion as described above for the synthesis of poly(1,4-phenylene terephthalamide). The amounts of intermediates used were 2.5183 g (0.022 mole) of 1,2-diaminocyclohexane, 5.65 ml of triethylamine, 1.93 g of lithium chloride, and 4.162 g (0.020 mole) of trans-hexahydroterephthalic acid chloride. Again the 1,2-diaminocyclohexane represented a 10 mole percent excess and the lithium chloride a 3.2 weight percent in solvent.

The above polyamidations were carried out consecutively. After 20 min, the residues in the two flasks were mixed together and stirred for 2 hr after which the block copolyamide, poly(1,2-cyclohexalene-trans-1,2-cyclohexane dicarboxamide: 1,4-phenylene terephthalamide) was collected and washed with water, acetone, dilute potassium hydroxide, dilute hydrochloric acid, and alcohol. It was dried in a vacuum oven at 220° for 24 hr.

Another batch of poly(1,2-cyclohexalene-trans-1,4-cyclohexane dicarboxamide) and poly(1,4-phenylene terephthalamide) was prepared as described above with the same amounts of reactants and solvent. After 20 min the poly(1,4-phenylene terephthalamide) with acid chloride end group was quenched with dilute potassium hydroxide, and the poly(1,2-cyclohexalene-trans-1,2-cyclohexane dicarboxamide) was quenched with dilute hydrochloric acid. These polyamides were isolated separately and washed with water, acetone, dilute potassium hydroxide, dilute hydrochloric acid, and alcohol. They were dried in a vacuum oven at 220° for 24 hr.

Poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate: 1,4-phenylene terephthalate).

Poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate: 1,4-phenylene terephthalate) was prepared by the condensation of a low molecular weight

poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) having terminal hydroxyl groups, and a low molecular weight poly(1,4-phenylene terephthalate) having acid chloride end groups.

Poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate): A low molecular weight poly(1,4-cyclohexalene-trans-hexahydroterephthalate) with terminal hydroxyl groups was prepared by placing 2.5556 g (0.022 mole) of 1,4-cyclohexane diol dissolved in 40 ml of dry o-dichlorobenzene into a 250 ml three-necked, round bottom flask equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap. To this stirred solution was added 4.1815 g (0.020 mole) of trans-1,4-cyclohexane dicarboxylic acid chloride. The reactor (the 250 ml round bottom flask containing the above materials) was purged continuously with nitrogen. The solution was heated at 85-110° for 45 min until almost all hydrogen chloride gas had been evolved. The solution was then brought to reflux for 2½ hr under nitrogen, after which the polymer solution was allowed to cool. The diol represented a 10 mole percent excess.

Poly(1,4-phenylene terephthalate): A low molecular weight poly(1,4-phenylene terephthalate) with terminal acid chloride groups was prepared using the same procedure as described above for the preparation of poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate). The amounts of reactants and solvent used were 4.4046 g (0.040 mole) of para-dihydroxybenzene (hydroquinone), 8.9332 g (0.044 mole) of terephthaloyl chloride, and 40 ml of dry o-dichlorobenzene. The terephthaloyl chloride represents a 10 mole percent excess of the equivalent amount of the hydroquinone.

After the two different polymer solutions had cooled, 20 ml of each of the solutions were thoroughly mixed and refluxed for 1 hr under a nitrogen atmosphere. The block copolyester, poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate: 1,4-phenylele terephthalate) was collected and washed with water, acetone, dilute potassium hydroxide, dilute hydrochloric acid, and alcohol. It was dried in a vacuum oven at 220° for 24 hr.

The rest of the two different polyester solutions were isolated and washed with the same nonsolvents as mentioned above. They were dried at 220° for 24 hr in a vacuum oven.

Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate: 2-methyl-1,3-phenylene terephthalate).

Poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate: 2-methyl-1,3-phenylene terephthalate) was prepared by coupling a low molecular weight poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) having terminal hydroxyl groups and a low molecular weight 2-methyl-1,3-phenylene terephthalate polyester having hydroxyl end groups, with a small amount of terephthaloyl chloride.

Poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate): An oligomer of 1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate with hydroxyl end groups was prepared by placing 4.7087 g (0.022 mole) of trans-1,4-cyclohexanedicarboxylic acid chloride dissolved in 20 ml of dry o-dichlorobenzene into a 100 ml, three-necked, round bottom flask equipped with a magnetic stirrer, condenser, a nitrogen inlet, and a potassium hydroxide trap. To this was added 2.8743 g (0.0247 mole) of 1,4-cyclohexane diol. With a nitrogen sweep the stirred mixture was heated at 90-100° for 50 min until almost all hydrogen chloride gas had been liberated (litmus paper

test). The temperature was then increased and the solution was refluxed for 2½ hr under nitrogen, after which it was cooled. The above amount of 1,4-cyclohexane diol represented a 10 mole percent excess.

Poly(2-methyl-1,3-phenylene terephthalate): A low molecular weight polyterephthalate of 2-methylresorcinol with terminal hydroxyl groups was also prepared in a similar manner as described for the poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate). The amounts of monomers and solvent employed were 5.4805g (0.044 mole) of 2-methylresorcinol and 8.1371 g (0.040 mole) of terephthaoyl chloride dissolved in 40 ml of dry o-dichlorobenzene. After refluxing for 2½ hr, the solution was allowed to cool into a creamy colored solid.

After the above two polyesters had been warmed until a complete liquid phase was observed, about 10 ml of each of the polyester solutions were mixed thoroughly with a magnetic stirrer and a stream of nitrogen. The mixture was heated at reflux for 45 min and 0.63481 g of terephthaloyl chloride was carefully introduced. The mixture was refluxed for another 30 min and then cooled. The block copolyester, poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate: 2-methyl-1,3-phenylene terephthalate) and the aliphatic and aromatic polyesters were isolated separately and washed with acetone, water, dilute potassium hydroxide, dilute hydrochloric acid and alcohol. Before washing, the poly(1,4-cyclohexalene-trans-1,4-cyclohexanedioate) was poured into about 50 ml of acetone and allowed to stand for 3 days. The polyesters and block copolyester were dried in a vacuum oven at 195° for 24 hr.

Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate : 2-methyl-1,3-phenylene isophthalate)

. Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate: 2-methyl-1,3-phenylene isophthalate) was prepared by two methods. The first method involved blocking poly(2-methyl-1,3-phenylene isophthalate) having terminal hydroxyl groups and poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) having terminal hydroxyl groups with an acid chloride. The acid chloride employed as a coupling agent was isophthaloyl chloride. The second method employed was the condensation of poly(trans-1,2-cyclohexalene-trans-1,4-cyclohexanedioate) having hydroxyl end groups with poly(2-methyl-1,3-phenylene isophthalate) having terminal acid chloride groups.

First Method - Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate): A low molecular weight poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) with hydroxyl end groups was prepared by adding 15.5281 g (0.0743 moles) of trans-hexahydrophthaloyl chloride dissolved in 70 ml of dry o-dichlorobenzene into a 250 ml round bottom, three-necked flask equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap. To this solution was added 9.50348 g (0.0817 mole) of trans-1,2-cyclohexane diol (Pfaltz and Bauer). The flask was purged with nitrogen. The solution was then heated around 110° for 45 min with evolution of hydrogen chloride gas. At atmospheric pressure and in a slow stream of nitrogen, the temperature was raised until refluxing was observed. At refluxing, a drying tube was employed to prevent possible introduction of moisture. After 5½ hr of refluxing, the solution was

allowed to cool. The amount of trans-1,2-cyclohexane diol was 10 mole percent in excess of the equivalent amount of trans-hexahydrophthaloyl chloride. Twenty-five ml of the polymer solution was put aside for use in the preparation of the block copolyester. The remaining solution was subjected to vacuum distillation wherein o-dichlorobenzene was distilled off at 86° (4 mmHg) and completely evacuated at 240° (polymer melt temperature). Distillation was stopped and the viscous polymer melt was allowed to cool into a tough solid.

Poly(2-methyl-1,3-phenylene isophthalate): An oligomer of 2-methyl-1,3-phenylene isophthalate with terminal hydroxyl groups was synthesized by adding 11.9371 g (0.0588 mole) of isophthaloyl choride dissolved in 45 ml of dry o-dichlorobenzene into a 250 ml round bottom, three-necked flask equipped with a nitrogen inlet, a magnetic stirrer, a condenser, a thermometer, and a potassium hydroxide trap. The stirred solution was heated to about 60°. To it was added 8.06134 g (0.065 mole) of 2-methylresorcinol. The temperature was brought up to 100° while the reactor was constantly purged with nitrogen. The temperature was maintained at 100° for 1 hr to give time for liberation of hydrogen chloride gas. The solution was refluxed for 5½ hr and then allowed to cool into a viscous solution. Twenty-five ml of the polymer solution was saved for preparing the block copolyester and the rest was isolated. The above amount of 2-methylresorcinol represented a 10 mole percent excess.

In an effort to isolate the polyisophthalate of 2-methylresorcinol vacuum distillation was used. The o-dichlorobenzene was distilled off at 86° (4 mmHg). A stream of nitrogen was passed continuously to assure an atmosphere free of oxygen or air. The o-dichlorobenzene was thoroughly evacuated when the temperature of

the polymer melt was 240°. Distillation was stopped and the viscous polyester melt was allowed to cool into a very tough orange solid.

In preparing the block copolyester poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate), 25 ml each of the unisolated poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) and poly(2-methyl-1,3-phenylene isophthalate) were thoroughly mixed under nitrogen. The mixture was refluxed for 20 min after which 1.203 g of isophthaloyl chloride was carefully introduced. Refluxing was resumed for another 2½ hr after which the solution was allowed to cool. The o-dichlorobenzene was distilled off at 86° (4 mmHg) and thoroughly evacuated at 240° (temperature of the polymer melt). The viscous block copolyester melt solidified into a very tough, dark tan product on cooling.

Second Method - Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate): A low molecular weight trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate polyester with terminal hydroxyl end groups was prepared by placing 15.3808 g (0.0736 mole) of trans-1,2-cyclohexane dicarboxylic acid chloride dissolved in 55 ml of dry o-dichlorobenzene into a 250 ml round bottom, three-necked flask equipped with a magnetic stirrer, condenser, a thermometer, a nitrogen inlet, and a potassium hydroxide trap. The stirred solution was heated to 40°. To this heated solution, with a constant nitrogen bleed-in, was added 9.39805 g (0.0892 mole) of trans-1,2-cyclohexane diol. The temperature of the mixture was brought up to 115° and maintained at this temperature for 1 hr while hydrogen chloride was evolved. The solution was heated at reflux for 7½ hr after which it was allowed to cool. From the polymer solution was removed 20 ml of solution for

use in the synthesis of the block copolymer. The o-dichlorobenzene was distilled off at 86° (4 mmHg) and thoroughly evacuated at 230° (polymer melt temperature). Distillation was discontinued and the viscous polyester melt solidified into a tough orange solid. The amount of trans-1,2-cyclohexane diol was a 10 mole percent excess.

Poly(2-methyl-1,3-phenylene isophthalate): An oligomer of 2-methyl-1,3-phenylene isophthalate was prepared. A 250 ml three-necked, round bottom flask equipped with a condenser, a magnetic stirrer, a nitrogen inlet, a thermometer, and a potassium hydroxide trap was charged with 13.8093 g (0.0683 mole) of isophthaloyl chloride dissolved in 45 ml of dry o-dichlorobenzene. To this stirred solution, with a continuous stream of nitrogen passing through, was added 7.7053 g (0.0621 mole) of 2-methylresorcinol. The temperature was raised to 115° and maintained for 1 hr with liberation of hydrogen chloride. The solution was refluxed for 7 hr and then allowed to cool. Twenty ml was removed for the synthesis of the block copolyester. The remaining solution was subjected to vacuum distillation wherein o-dichlorobenzene was distilled off at 86° (4 mmHg) and was thoroughly evacuated at 250° (polymer melt temperature). Distillation was terminated and the melt solidified. The amount of isophthaloyl chloride was 10 mole percent in excess of the equivalent amount of 2-methylresorcinol.

Synthesis of the block copolyester, poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) was accomplished by mixing thoroughly, with a nitrogen sweep, 20 ml each of poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) and poly(2-methyl-1,3-pheny-

lene isophthalate). The mixture was refluxed for 2½ hr after which it was allowed to cool. The o-dichlorobenzene was removed by vacuum distillation at 86° (4 mmHg). Complete evacuation was achieved at 230° (temperature of polymer melt). Distillation was stopped and the viscous block copolyester solidified into a very hard and tough polymer.

Poly(cis-1,2-cyclohexalene-cis-1,2-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate)

Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate): was synthesized by reacting a low molecular weight poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate) having terminal hydroxyl groups with a 2-methyl-1,3-phenylene isophthalate oligomer having acid chloride end groups.

Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate): An oligomer of cis-1,2-cyclohexalene-cis-hexahydrophthalate with terminal hydroxyl end groups was prepared. The monomer, cis-hexahydrophthalic acid chloride (12.069 g, 0.0557 mole) was dissolved in 43 ml of dry o-dichlorobenzene in a 250 ml round bottom, three-necked flask equipped with a magnetic stirrer, a condenser, a thermometer, a nitrogen inlet, and a potassium hydroxide trap. The mixture was heated to about 40° and 7.3771 g (0.0635 mole) of powdered cis-1,2-cyclohexane diol was added with stirring and a constant nitrogen bleed-in. The temperature was raised to 115° where it was maintained for 1 hr with evolution of hydrogen chloride. The mixture was then refluxed for 7½ hr after which it was allowed to cool. The above amount of cis-1,2-cyclohexane diol was 10 mole percent in excess of the equivalent amount of cis-hexahydrophthaloyl chloride. Twenty-five ml of the polymer solution was

removed (with minimum exposure to moisture) for the synthesis of the block copolyester. The remaining solution was vacuum distilled and o-dichlorobenzene was distilled off at 86° (4 mmHg) and completely evacuated at 200° (polymer melt temperature). Distillation was stopped and the viscous melt was allowed to solidify on cooling.

Poly(2-methyl-1,3-phenylene isophthalate): A low molecular weight poly(2-methyl-1,3-phenylene isophthalate) with acid chloride end groups was prepared. Into a 250 ml round bottom, three-necked flask equipped with a condenser, a magnetic stirrer, a nitrogen inlet, a thermometer, and a potassium hydroxide trap was added 13.8104 g (0.0683 mole) of isophthaloyl chloride dissolved in 50 ml of dry o-dichlorobenzene. To this stirred solution was added 7.7048 g (0.0621 mole) of 2-methylresorcinol. The flask was continually purged with nitrogen. The mixture was heated at 115° for 1 hr with liberation of hydrogen chloride. It was then refluxed for 8 hr after which it was allowed to cool. The amount of isophthaloyl chloride represented a 10 mole percent excess of the equivalent amount of the 2-methylresorcinol. From the polymer solution was removed 20 ml for use in the preparation of the block copolyester. The remaining solution was subjected to vacuum distillation whereby o-dichlorobenzene was distilled off at 86° (4 mmHg) and was completely evacuated at 250° (polymer melt temperature). Distillation was discontinued and the melt solidified on cooling.

In preparing the block copolyester poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 25 ml each of the poly(2-methyl-1,3-phenylene isophthalate) and poly(cis-1,2-cyclohexalene-cis-cyclohexane-1, 2-dicarboxylate) were mixed thoroughly. At atmospheric pressure

and in a slow stream of nitrogen, the temperature was raised until refluxing was observed for 7 hr. The solution was allowed to cool and then subjected to vacuum distillation. The o-dichlorobenzene was distilled off at 86° (4 mmHg) and was thoroughly evacuated at 230° (polymer melt temperature). Distillation was terminated and the viscous block copolyester melt solidified into a very tough and hard solid on cooling.

RESULTS & DISCUSSION

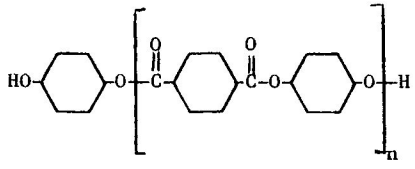
Our interest was to prepare linear polyamides and polyesters; more particularly, polyamide and polyester block copolymers. These polymers and their corresponding block copolymers are shown in Figure 1. The codes used do not in any way entail conventional representations for these prepolymers and block copolymers. They are employed only to avoid continuously writing lengthy names.

Synthesis

The preparation of the prepolymers and the block copolymers can be accomplished by either melt polymerization or solution polymerization. We used solution polymerization because polymerization of monomers in a solvent alleviates some of the problems that one encounters with polymerizations.[8-10] The monomers are diluted by the inert solvent which helps in the transfer of the heat of polymerization. Stirring is easily accomplished in the presence of the solvent since the viscosity of the reaction mixture is decreased. Thermal control is also much more easily maintained in solution polymerization as compared to bulk polymerization. The difficulty which may be encountered with solution polymerization, if the solvent is chosen without appropriate considerations, is the removal of the solvent. This may be difficult, dangerous and expensive, and may affect the purity of the polymer.

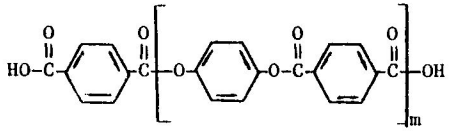
The methods[8] associated with the preparation of polyamides through step-growth process are (a) polycondensation of ω-amino acids, (b) polycondensation of diamines with dicarboxylic acids, (c) polycondensation of diamines with diacid

CODES



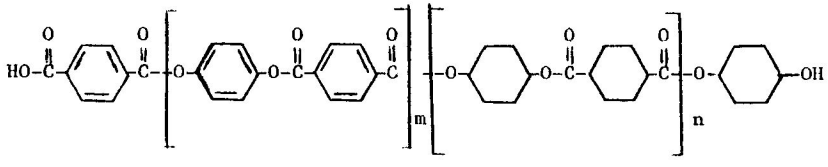
1-PEAL-1

Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate)



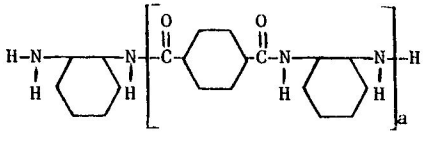
1-PEAR-1

Poly(1,4-phenylene terephthalate)



1-PEBL-1

Poly(1,4-cyclohexalene-1,4-cyclohexanedioate : 1,4-phenylene terephthalate)

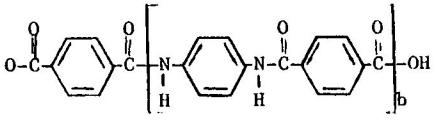


2-PAAL-1

Poly(1,2-cyclohexalene-1,4-cyclohexanedicarboxamide)

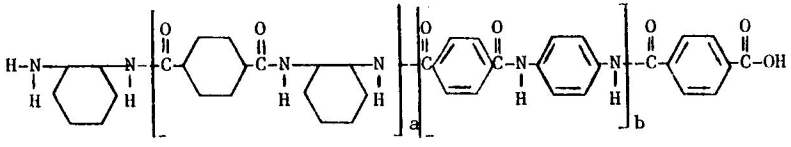
Fig. 1. Codes, names and structures of synthesized prepolymers and block copolymers.

CODES



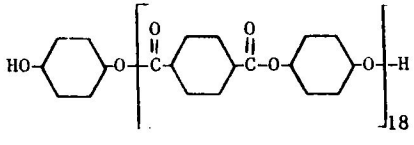
2-PAAR-1

Poly(1,4-phenylene terephthalamide)



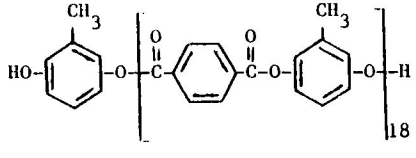
2-PABL-1

Poly(1,2-cyclohexalene-1,4-cyclohexanedicarboxamide : 1,4-phenylene terephthalamide)



3-PEAL-1

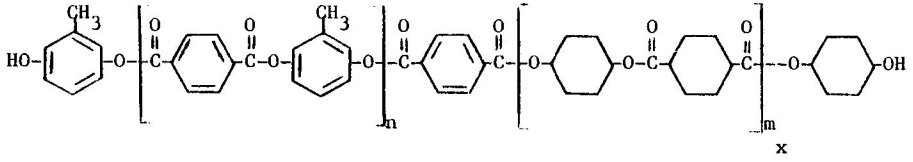
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate)



3-PEAR-1

Poly(2-methyl-1,3-phenylene terephthalate)

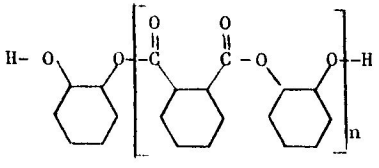
Fig. 1 (Continued).



CODES

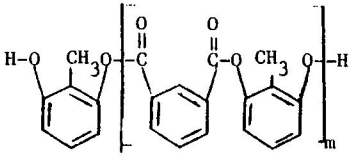
3-PEBL-1

Poly(1,4-cyclohexalene-1,4-cyclohexanedioate : 2-methyl-1,3-phenylene terephthalate)



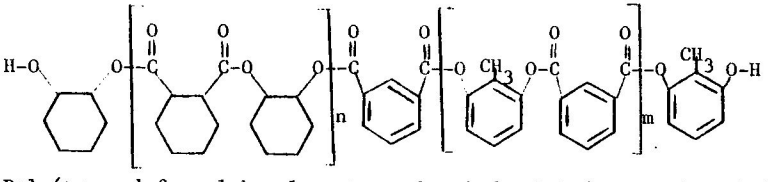
4-PEAL-1

Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate)



4-PEAR-1

Poly(2-methyl-1,3-phenylene isophthalate)



4-PEBL-1

Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate : 2-methyl-1,3-phenylene terephthalate)

Fig. 1 (Continued).

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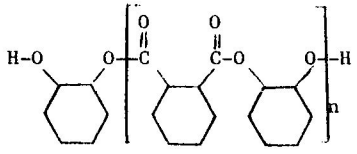
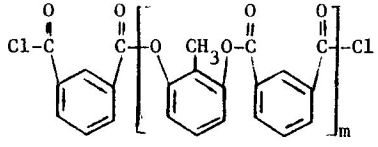


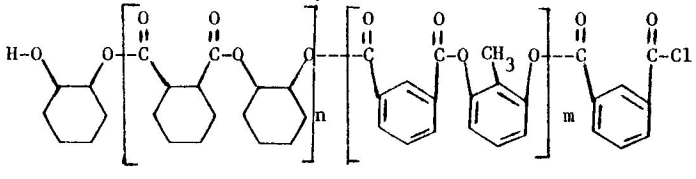
4-PEAL-2

Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate)



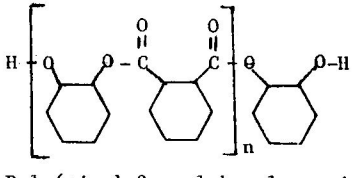
4-PEAR-2

Poly(2-methyl-1,3-phenylene isophthalate)



4-PEBL-2

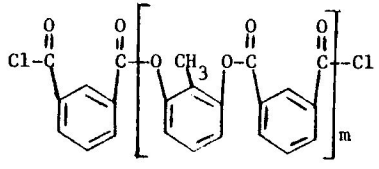
Poly(trans-1,2-cyclohexalene-trans-hexahydrophthalate; 2-methyl-1,3-phenylene isophthalate)



5-PEAL-1

Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate)

Fig. 1 (Continued).



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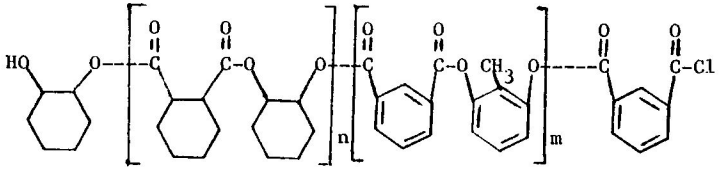
5-PEAR-1

Poly(2-methyl-1,3-phenylene isophthalate)



5-PEBL-1

Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate)

Fig. 1 (Continued).

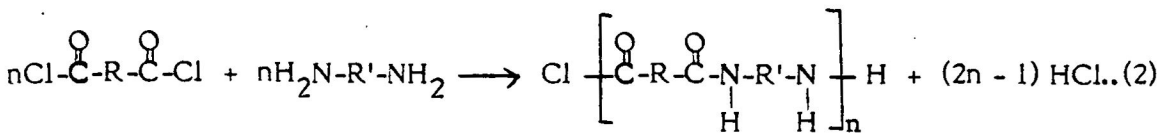
halides, and (d) ring-opening polymerization of cyclic amides (lactam). We eliminated methods (a) and (d) because they will not yield the polymers of interest. Method (b) requires high temperature heating and elimination of by-products which might pose some problems. Method (c) was employed because the most significant polymerization process for the polyamides is the low-temperature polycondensation of diamines with diacid chlorides in an amide type solvent in the presence of added salt.[11,12] The salt is supposed to facilitate the solvation of the polyamides in the liquid medium. Low temperature reactions[13] are also desirable for economy and they reduce by-product formation and promote linear polyamide formation. The diamines and diacid chlorides were used because, in the absence of heating, they are the most reactive intermediates in the preparation of polyamides; on the other hand, minimum exposure to moisture must be observed since the diacid chloride is susceptible to hydrolysis and to interaction with a solvent medium.

For the polyesters, these methods can be used: (a) polycondensation of hydroxy acids, (b) polycondensation of diols with dicarboxylic acids or dimethyl esters, (c) polycondensation of diols with diacid halides, and (d) ring opening polymerization of cyclic esters (lactones). The criteria responsible for the elimination of methods (a), (b) and (c) for polyamidation are also responsible for polyesterification. The diols and diacid chloride were used for polyesterification because they are the most reactive intermediates for polyester formation. The diacid chloride is also prone to hydrolysis and care must be exercised not to expose it to moisture for a long time. Unlike polyamidation where low-temperature polycondensation is employed, heating is required for polyesterification. This is explained by the fact that most polyamidation processes, using diamines and diacid

chlorides, are exothermic due to the high reactivities of these intermediates. Polyesterifications involving diols and diacid chlorides require a higher activation energy compared to polyamidation involving diamines and diacid chlorides, and therefore require heating. Most polyesterification processes are endothermic. In the polyesterification, as in most other high temperature polycondensation reactions, an inert gas is almost routinely employed to initially purge a reactor vessel or to continuously blanket or sweep a polymerization system. The purpose of using the inert gas, nitrogen, was to minimize oxidation which would cause degradation of the polymer or reactants.[9,14] The nitrogen was also employed to help drive off the by-product, hydrogen chloride,and prevent it from accumulating in the system. As aforementioned, for both the polyesterification and polyamidation processes, moisture should be excluded as much as possible when the condensation takes place through acid chloride end groups, especially in the blocking step, since moisture will cause hydrolysis of the acid chloride to yield a free acid and a resultant reduction in reaction rate.

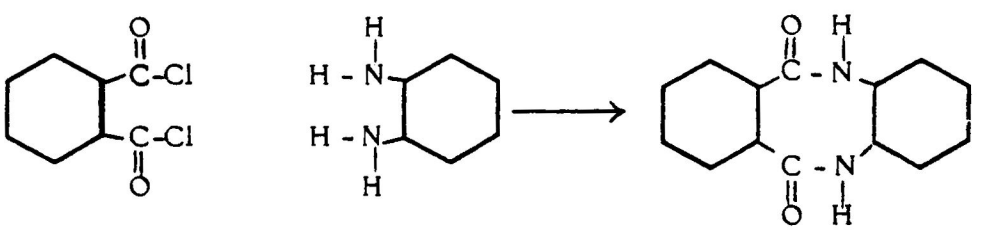
The by-product in the formation of the polyamides, polyesters, block copolyamide, and block copolyester was hydrogen chloride. This was trapped with triethylamine in the case of the low temperature polyamidation, and with a potassium hydroxide trap connected through a condenser to the polymerization system in the case of the high temperature polyesterification. Most step-growth processes[8,10] are equilibrium processes, as given for example, in equations (1) and (2) below.

$$n\text{Cl-}\overset{\overset{O}{\|}}{\text{C}}\text{-R-}\overset{\overset{O}{\|}}{\text{C}}\text{-Cl} + n\text{HO-R'-OH} \longrightarrow \text{Cl}\left[\overset{\overset{O}{\|}}{\text{C}}\text{-R-}\overset{\overset{O}{\|}}{\text{C}}\text{-O-R'-O}\right]_n\text{H} + (2n-1)\,\text{HCl} \quad \ldots \quad (1)$$



Elimination of the by-product shifts the equilibrium to the right, and thereby to high molecular weight products. If the by-product were not eliminated, the polymerization rate might be hindered and low molecular weight product attained. It has also been found[10] that the equilibrium for amidation reactions is much more favorable than for the esterification reactions. It is for this reason that some polyamidations are carried out without concern for shifting the equilibrium until the last stages of reaction.

Attempts were made to prepare poly(1,2-cyclohexalene-cis-cyclohexane1,2-dicarboxamide: 1,4-phenylene 4-methlyphthalamide) in N,N-dimethylacetamide and N-methylpyrrolidone. The preparation of the poly(1,4-phenylene 4-methylphthalamide) with acid chloride end groups in N,N-dimethylacetamide was successful because the polymer remained in solution and could be precipitated by pouring into a stirred excess of a nonsolvent such as hexane. The preparation of the poly(1,2-cyclohexane-cis-cyclohexane-1,2-dicarboxamide) in N,N-dimethylacetamide was unsuccessful because attempts to precipitate the polymer failed. The supposed aliphatic polyamide was soluble in water, acetone, hexane, and alcohol. Its solubility in water and other polyamide nonsolvents suggested that it is not a polymer. It may have been that the monomers did not react due to a problem of architectural deficiency. Formation of the polymer may have been energetically unfavorable due to the proximity of the functional groups; or the monomers may have reacted to give:



Attempts to polymerize the same monomers in N-methylpyrolidone resulted in immediate precipitation. This made it impossible to couple the two different polyamides. Preparation of poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 1,4-phenylene terephthalate) was also unsuccessful.

High molecular weight poly(1,4-phenylene terephthalamide) has been prepared.[12,15-19] The same procedure may be employed to prepare the polyamides used in formation of the block copolyamide. Poly(1,4-phenylene terephthalate) has been prepared,[20] but attainment of high molecular weight in polyarylates is not easily achieved.

A look at all the aliphatic components of the block copolyesters and block copolyamide reveals the presence of sterically hindered ester and amide groups respectively. It has been found[2,21-23] that polyesters which are characterized by the presence of sterically hindered ester groups are less susceptible to randomization reactions than those which are characterized by the presence of non-hindered ester groups. It has also been maintained that relatively low molecular weight, sterically hindered polyesters may react preferentially at their terminal groups rather than by ester interchange reactions, thereby allowing the formation of block copolymer. For the polyamides, the presence of a sterically hindered amide group is good but not necessary, since the method of low-temperature polycondensation is employed. Randomization is seldom observed for this method.

In the preparation of the polyesters, either the acid chloride or the diol was in excess of the equivalent amount of the other, and in the polyamide preparations, either the acid chloride or the diamine was in excess. This technique was employed for the purpose of synthesizing polymers with known functional end groups. In

synthesizing the block copolyesters, two methods were used. The first method involved the preparation of the aliphatic polyesters with hydroxyl end groups, and the aromatic polyesters with terminal acid chloride groups, then coupling the polyesters by merely allowing them to react from their end groups. The second method involved the preparation of both the aliphatic and aromatic polyesters with terminal hydroxyl groups, and then coupling them with an acid chloride. The second method could also have been employed for the polyamide formation by preparing both the aliphatic and the aromatic polyamides with amino end groups, and then coupling them with an acid chloride.

It is also possible to prepare polyesters and polyamides, with acid chloride end groups, which are then coupled by a diol and a diamine, respectively. This was not employed since acid chlorides are highly susceptible to hydrolysis. If the end groups of these polymers would hydrolyze before the coupling stage, then formation of the blocks would be impossible. The polyesters and polyamides could also have been prepared with terminal hydroxyl and amino groups respectively, and then coupled by reacting both polyesters or both polyamides with a bifunctional compound such as a diisocyanate, a diisothiocyanate, or other coupling agents with a sufficiently fast rate of reaction to minimize ester or amide interchange. The effect of the urethane or the thiocyanate linkage can, in most cases, be neglected but it is also true that these linkages are capable of distorting the polyester or polyamide structure to some extent and can alter their crystallizability.

Characterization

Characterization of block copolymers presents much more difficulty than characterization of homopolymers, and so an unequivocal determination of the structure of a block copolymer is a formidable task. As a result, a majority of block copolymers reported in the literature are not well characterized. The only block copolymer that has received extensive characterization is the styrene-diene block copolymer because it is prepared by a controllable anionic living polymerization process. In most cases, block copolymers have been assigned structures deduced almost solely from the synthetic procedure employed.

Generally[24-29] characterization of homopolymers, prepolymers, and block copolymers is achieved by elemental analysis, solubility, solution viscosity, melt viscosity, average molecular weight, molecular weight distributions, degree of crystallinity, spectroscopic techniques (infra-red, proton and carbon-13 nuclear magnetic resonance) and thermal analysis (differential scanning calorimetry and thermal gravimetric analysis). Sometimes, the mechanism of the polymerization is employed concertedly. But even when all these approaches are used, the block copolymer structure sometimes remains questionable. One is also often faced with the problem of determining whether a given reaction product is a block copolymer, random copolymer, or just mere homopolymer blends (a physical mixture of the prepolymers).

The properties of copolymers depend not only on the chemical nature of the counits but also on their segmental arrangement along the chain. It has been mentioned previously that block copolymers have additive properties of the individual homopolymers or prepolymers constituting the block. So it is possible to

synthesize block copolymers which have desirable properties characteristic of each of the corresponding homopolymers incorporated into a single molecular chain. Contrary to this property displayed by block copolymers, random and alternating copolymers usually exhibit properties that are considerably different from those of corresponding homopolymers. In some cases, the properties have been shown to be a weighted average of the respective prepolymers. It is possible, sometimes, to differentiate among copolymers by their properties.

The question as to whether a reaction product is a copolymer or merely a homopolymer blend is answered by solubility behavior. Homopolymer blends and copolymers show different responses to extraction with selective solvents and to solvent-nonsolvent fractionation techniques like fractional precipitation, column fractionation, and turbidometric titrations. These methods work very well for systems that have different chemical structures and/or physical states such as polar-nonpolar and crystalline-amorphous. However, it is possible to find a block copolymer which is soluble in a solvent that does not dissolve either of the corresponding homopolymers, or is incapable of dissolving one of the homopolymers.

The differentiation between a block and random copolymer can be ascertained by the use of proton and carbon-13 nuclear magnetic resonance spectroscopy, infrared spectroscopy, dynamic mechanical analysis, differential scanning calorimetry (DSC), microscopy, and x-ray crystallography. Block copolymers have additive properties of the corresponding prepolymers and therefore will show data that are characteristic of the individual components, while random copolymers give

an average value of the corresponding prepolymers.

Infrared spectra for the block copolymers synthesized and blends of the corresponding prepolymers showed that the reaction products were truely block copolymers. This was determined by the proportion of the end group stretches to the carbonyl stretches in each case. Since the blends have twice as much end groups as the block copolymer they were expected to have broader peaks compared to that of the block copolymers.

In DSC, the differential heat flow between a sample and a reference is plotted as a function of sample temperature. The glass transition temperature (T_g) is shown as a change in base-line slope corresponding to a change in specific heat for a second-order thermodynamic transition, while a melting transition (T_m) corresponding to a first-order transition is indicated by an endotherm.[29-32]

The glass transition temperature (T_g)[33-35] is the temperature below which the polymer is hard and glassy, while above it, the polymer if sufficiently high in molecular weight, behaves as a rubber or leather. As the temperature increases the polymer becomes a highly viscous liquid. T_g is a parameter that defines the properties of a homopolymer or copolymer. After the polymer has gone to the rubbery state, the chains must be able to sample all the available conformations, be flexible, tough, and highly deformable. In the glassy state it is rigid, very brittle and easily fractured. Although the glassy state and rubbery state clearly represent opposite extremes in mechanical properties in both cases, the chains are in a statistical conformation. Thus, the differences exhibited by the properties of the two states do not stem from any fundamental difference in structure or molecular arrangement, but rather in the time scale of the sequential motions and their

response to external stress. The glass transition temperature is, in general, evidenced by a change in some physical property (e.g., expansion coefficient, specific volume, dynamic modulus of elasticity, heat capacity or dielectric constant) as the sample material is heated or cooled through the transition region. The glass transition temperature [35] varies slightly depending on the speed with which the measurement is made. In other words, the T_g is lower for a slowly cooled or heated material than for a rapidly cooled or heated material. This is seen to be true for the thermogram of poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate). The T_g obtained at a program rate of 10°/min was 60° and obtained at a program rate of 20°/min was 63°.

Factors affecting T_g are (a) regularity of structure, i.e. molecular symmetry, (b) stiff intrachain bonds, (c) linear chains capable of close packing, and (4) the presence of dipole interaction and polarization. The higher the degree of any of the above factors the higher the T_g. Experience has shown that it is much easier to explain a T_g value once it has been obtained than to predict it from the molecular structure of the material. For polymers with crystalline and amorphous regions a rule of thumb applies. The ratio of the glass transition temperature to the melting temperature, T_g/T_m, using absolute scale, lies between 0.4 and 0.8. For symmetrical polymers like polyethylene the ratio lies closer to 0.5 and to 0.7 for unsymmetrical polymers like polystyrenes, polyesters, polyamides, etc. Table 1 gives the values of T_g, T_m, and T_g/T_m for the synthesized prepolymers and block copolymers.

Table 1. Glass Transition and Melting Temperatures for the Polyesters, Polyamides, and Block Copolyesters and Block Copolyamide.

Polymer	T_g^o Program rate 20°/min	T_m^o Program rate 20°/min	T_m^o Program rate 50°/min	$(T_g/K)/(T_m/K)$
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) 1-PEAL-1	225	345	356	0.80
Poly(1,4-phenylene terephthalate) 1-PEAR-1	300	525	500	0.72
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate:1,4-phenylene terephthalate) 1-PEBL-1	235;-	345;-	352;511	0.82;-
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) 3-PEAL-1	225	350	362	0.80
Poly(2-methyl-1,3-phenylene terephthalate) 3-PEAR-1	282	315;437;455	330;455	
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate:2-methyl-1,3-phenylene terephthalate) 3-PEBL-1	213;-	363;438	360;433	0.76;-
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) 4-PEAL-1	58	278	286	0.60
Poly(2-methyl-1,3-phenylene isophthalate) 4-PEAR-1	103	460	480	0.57
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate:2-methyl-1,3-phenylene isophthalate)4-PEAR-1			313;480	

Table 1 (Continued).

Polymer	T_g^o Program rate 20°/min	T_m^o Program rate 20°/min	T_m^o Program rate 20°/min	$(T_g/K)/(T_m/K)$
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1, 2-dicarboxylate) 4-PEAL-2	63	282	288	0.61
Poly(2-methyl-1,3-phenylene isophthalate) 4-PEAR-2	230	474	474	0.67
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1, 2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 4-PEBL-2				
Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1, 2-dicarboxylate) 5-PEAL-1	62	282	285	0.60
Poly(2-methyl-1,3-phenylene isophthalate) 5-PEAR-1	230	320,470	482	0.68
Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1, 2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 5-PEBL-1	62;220	280;470	294;477	0.60;0.66
Poly(1,2-cyclohexalene-trans-cyclohexane-1, 4-dicarboxamide) 2-PAAL-1	122	435	454	0.56
Poly(1,4-phenylene terephthalamide) 2-PAAR-1	157	525	500	0.54
Poly(1,2-cyclohexalene-trans-cyclohexane-1, 4-dicarboxamide: 1,4-phenylene terephthalamide) 2-PABL-1	113;-	382;514	383;516	0.59;-

The melting temperature is the temperature of transition between the solid and liquid state. The same factors[36,37] as stated above governing T_g also govern T_m. Also, the program rate affects the value of the T_m as may be seen by the values given for poly(trans-1,2-cyclohexalene-trans-cyclohexane dicarboxylate). At a program rate of 50°/min, the value of T_m was 287°, but at a program rate of 20°/min, the T_m value was 280°. In general, lower program rates correspond to equilibrium value for the T_m.

Note that the extrapolated onset temperature is ordinarily used as the melting point.

Block copolymer behavior[27] is related to solid state morphology. Block copolymers frequently exhibit phase separation which typically gives rise to a dispersed phase consisting of one block type in a continuous matrix of the second block type. Hence, they generally exhibit properties that are analogous to those of the corresponding prepolymers. Therefore, each phase exhibits its normal, or near normal T_g or T_m. This is confirmed by Table 1. A closer look at the table reveals that block copolymers 1-PEBL-1, 2-PABL-1, and 3-PEBL-1 have melting temperatures lower than those of the corresponding prepolymers. This is because copolymerization lowers glass transition and melting temperatures. Block copolymers 4-PEBL-1 and 5-PEBL-1 can be seen to have deviated slightly from the general rule. Liquid-crystalline polymers[30,38,39] display more than one melting transition on a typical DSC scan.[30] For example, The DSC scan of the liquid crystal, 4-n-octyloxyphenyl 4-(4-n-octoloxybenzyloxy) benzoate (PBOB) shows multiple melt transitions in the temperature range 84° to 189°.[39] We observed such multiple transitions for poly(2-methyl-1,3-phenylene terephthalate). We

suspect this polymer to be a liquid crystal, but these liquid crystalline transitions would have to be confirmed by optical microscopy studies.

Another method of characterization that helps elucidate the block copolymer structure is the carbon-13 nuclear magnetic resonance.[40-42] Without actually identifying the individual peaks, Tables 2, 3, 4, and 5 are used to show that the reaction products are block copolymers since the additive properties (position of peaks) correspond to those of the individual prepolymers.

Table 2. Carbon-13 Nuclear Magnetic Resonance Spectral Data for Poly(1,2-cyclohexalene- trans-1,4-cyclohexanedicarboxamide: 1,4-phenylene terephthalamide) in Deuterated Sulfuric Acid, D_2SO_4.

PPM
154.578
154.384
146.306
108.166
107.234
107.001
106.690
105.137
104.360
101.136
100.709
100.010
18.487
16.251
16.002
1.515
1.049
0.000

As shown in Table 2, the peak at 146.306 ppm is due to the carbonyl carbons within the chain, and the peaks at 154.578 and 154.384 ppm are due to the carbonyl carbons of the terminal carboxyl groups. The region between 100.010 and 108.166 ppm represents the aromatic carbons in the aromatic segment of the block copolyamide. The values between 1.049 and 18.487 ppm belong to the aliphatic sequence in the block. The peak at 105.137 ppm is the solvent peak. The values for the carbons closer to the two nitrogens are expected to be found more downfield than those of the carbons closer to the carbonyls.

In Table 3, the peaks are seen to be a combination of the peaks for the aliphatic and aromatic prepolymers. The structure of the polyester block copolymer, poly(1,4-cyclohexalene-trans-cyclohexalene-1,4-dicarboxylate: 2-methyl-1,3-phenylene terephthalate), is shown in Figure 1.

The peaks at 175.039, 174.922 and 163.770 ppm are carbonyl carbon peaks. The region between 120.194 and 150.294 ppm represents the aromatic carbons, and the region between 27.423 and 69.792 ppm belongs to the aliphatic carbons. The peak at 10.210 ppm which appears in the block copolymer and not in the aliphatic prepolyester, is due to the carbon of the methyl group on the aromatic segment of the block. The spectrum for poly(2-methyl-1,3-phenylene terephthalate) was not obtained due to this compound's insolubility in chloroform. It was found that the areas (integral) under the peaks are smaller for the aromatic section than for the aliphatic segment. The peaks at 76.559, 77.089, and 77.589 ppm are solvent peaks.

From the data in Table 4, the chemical shifts for the aliphatic polyester, poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate), and the aromatic polyester, poly(2-methyl-1,3-phenylene isophthalate), are incorporated in

Table 3. Carbon-13 Nuclear Magnetic Resonance Spectral Data for Poly(1,4-cyclohexane-trans-cyclohexane-1,4-dicarboxylate) 3-PEAL-1, and Poly(1,4-cyclohexane-trans-1,4-cyclohexanedioate : 20 methyl-1,3-phenylene terephthalate) 3-PEBL-1 in Deuterated Chloroform, $CDCl_3$ with 1% TMS.

3-PEAL-1 ppm	3-PEBL-1 ppm
175.01	175.039
174.892	174.922
	163.770
	150.294
	130.551
	126.962
	120.194
77.589	77.589
77.089	77.089
76.589	76.559
70.528	70.557
69.792	69.822
42.782	42.782
	29.217
28.394	28.953
28.099	28.099
27.687	27.746
27.423	27.423
0.000	0.000

Table 4. Carbon-13 Nuclear Magnetic Resonance Spectral Data for Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) 4-PEAL-2, Poly(2-methyl-1,3-phenylene isophthalate) 4-PEAR-2, and Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate), 4-PEBL-2 in $CDCl_3$ with 1% TMS.

4-PEAL-2 ppm	4-PEAR-2 ppm	4-PEBL-2 ppm
174.304		174.480
174.039		174.216
	163.741	163.711
	150.265	150.235
	135.877	135.230
	135.230	131.934
	131.993	130.110
	130.640	129.463
	130.169	126.932
	129.757	123.902
	129.463	120.135
73.853	126.962	73.235
73.264	123.931	44.635
44.665	120.165	42.723
42.340		42.517
29.835		42.399
28.894		42.311
26.098		40.457
25.216		29.894
24.774		28.835
23.745		26.128
23.186		25.186
22.391		23.686
21.450		23.156
19.831	10.210	21.950
0.000	0.000	21.302
		10.210
		9.121
		0.000

the chemical shifts for the polyester block copolymer, poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate). The peaks at 174.480 and 174.216 ppm (from 4-PEBL-2 chemical shifts) represents the carbonyls of the aliphatic polyester, and that at 163.711 ppm represents the carbonyls of the aromatic polyester. The chemical shifts between 120.135 and 150.235 ppm are due to the carbons of the aromatic polyester, and those between 9.121 and 73.235 ppm (except 10.210 ppm which is due to the carbon of the methyl group in the aromatic polyester) are due to the carbons of the aliphatic polyesters. In the chemical shifts for 4-PEAL-2 only one value (42.340 ppm) is seen around 42 ppm but for 4-PEBL-2, four values (42.311, 42.399, 42.517, and 42.723 ppm) are seen. This may be due to the presence of the covalent bond between the aliphatic and aromatic polyesters causing some splitting. The peaks at 76.618, 77.148 and 77.648 ppm, due to the solvent ($CDCl_3$), have been left out for convenience.

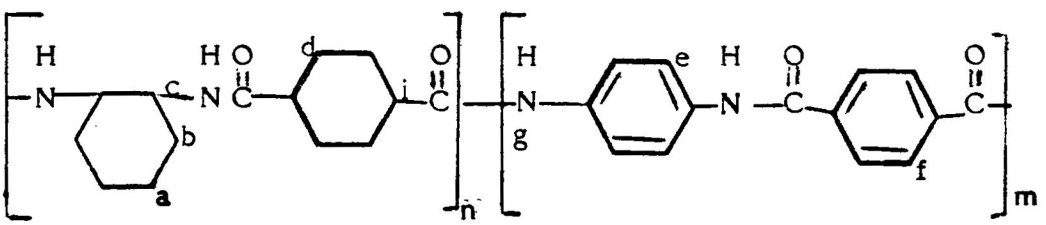
In Table 5 are displayed the chemical shifts for the polyesters, 5-PEAL-1, 5-PEAR-2, and the block copolyester, 5-PEBL-1.

Also in Table 5, it can be seen that chemical shifts of the individual polyesters are incorporated in the block copolyester at the normal, or near normal positions. The chemical shifts at 173.921 and 172.744 ppm, in the block copolyester, belong to the carbons of the aliphatic polyester segment, and the shift at 163.682 ppm belongs to the carbonyl carbon of the aromatic polyester segment. The region of chemical shifts between 120.135 and 150.235 ppm represents the carbons in the aromatic polyester; poly(2-methyl-1,3-phenylene isophthalate) and

the shifts between 20.832 and 75.824 ppm represent the carbons of the aliphatic polyester, poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylene). The chemical shift at 10.210 ppm is due to the carbon of the methyl group on the aromatic section of the polyester block copolymer, poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate). The chemical shifts at 77.619, 77.199, and 76.618 ppm are due to the carbon in the solvent $CDCl_3$.

A careful look at Tables 4 and 5 shows that the values of chemical shifts for polyesters 4-PEAR-2 and 5-PEAR-1 are the same. This may not be surprising since the aromatic polyesters are the same polyester prepared separately. These two tables also reveal that almost all chemical shifts observed for the polyesters in Table 4 are observed for those in Table 5.

Another method utilized in elucidating polymer structure is proton nuclear magnetic resonance spectroscopy. The chemical shifts in Table 6 are explained using the structure of the polyamide block copolymer shown below.



In Table 6, the chemical shift at 10.330 ppm is due to the solvent, and that at 7.991 ppm is due to the secondary amide protons (g) in the block copolymer. The chemical shifts at 7.824 and 7.722 ppm are due to the four equivalent aromatic protons (e) between the nitrogens since they are deshielded, and those peaks at 7.450 and 7.248 ppm represent the resonances of the aromatic protons (f) between the carbonyls. The amino groups deshield more efficiently than the carbonyl

Table 5. Carbon-13 Nuclear Magnetic Resonance Spectral Data for 5-PEAL-1, Poly (cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate); 5-PEAR-1, Poly(2-methyl-1,3-phenylene isophthalate); and 5-PEBL-1, Poly(cis-1,2-cyclohexane-cis-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate) in $CDCl_3$ with 1% TMS.

5-PEAL-1 ppm	5-PEAR-1 ppm	5-PEBL-1 ppm
180.777		173.921
179.600		172.744
174.098	163.682	163.682
173.892	150.235	150.235
172.833	136.583	135.200
	135.200	131.934
	131.934	130.110
	130.581	129.433
	130.139	126.903
77.648	129.433	123.902
77.119	127.785	120.135
76.618	126.903	77.619
75.824	123.902	77.119
73.058	120.135	76.618
71.204	120.135	75.794
60.759	77.560	71.175
60.112	77.060	60.789
44.841	76.559	60.171
42.428		44.841
34.867		42.693
		34.808
30.718		31.071
29.806		29.982
28.953		29.011
27.717		27.717
26.040		26.187
25.245		25.245
24.568		24.568
23.892		23.892
23.215		23.244
21.714	10.210	21.685
20.832	0.000	20.832
0.000		10.210
		0.000

groups. The band at 3.036 ppm represents the resonance of the methine groups (c) near the nitrogens, and that at 2.254 ppm is due to the methine hydrogen (i) near the carbonyls. The chemical shift at 1.694 ppm corresponds to the methylene group (b), and that at 1.156 ppm corresponds to the methylene groups (d) between the carbonyls in the aliphatic ring. The peak at 0.878 ppm is due to the methylene group (a).

Table 6. Proton NMR Spectrum of Poly(1,2-cyclohexalene-trans-cyclohexane-1, 2-dicarboxamide : 1,4-phenyl terephthalamide) in D_2SO_4.

PPM
10.330
7.991
7.824
7.722
7.450
7.248
3.036
2.254
1.694
1.156
.878

In Table 7, the chemical shifts at 8.329 and 8.316 ppm correspond to the four equivalent aromatic protons (a) as shown below:

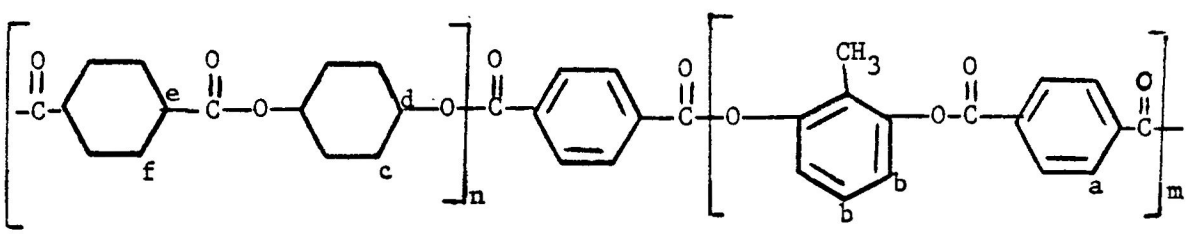


Table 7. Proton NMR Spectrom of Poly(1,4-cyclohexalene-trans-cyclohexane-1, 4-dicarboxylate : 2-methyl-1,3-phenylene terephthalate) in $CDCl_3$.

ppm	Integral
8.329	1.166
8.316	.868
7.215	.296
7.200	1.609
4.755	6.603
2.202	8.446
2.111	.478
2.080	1.045
2.065	1.696
1.983	13.255
1.885	3.051
1.851	5.121
1.667	17.898
1.478	6.656
1.432	3.358
1.392	11.853
1.192	3.904
.000	2.983

The peaks at 7.215 and 7.200 ppm are due to the hydrogens (b), which appear as a singlet. One may have anticipated a more complex absorption in this region because of the expectation that the meta and para hydrogens would have different chemical shifts and would therefore couple to one another so as to produce a complex spin-spin splitting pattern. The chemical shift difference in the above example is actually quite small so that the overall behavior is that for three equivalent protons. The peaks between 1.192 and 2.002 ppm belong to a complex splitting pattern of the methine and methylene groups (d, e, c, f). The methine hydrogens are expected to appear more downfield than the methylene groups.

In Table 8 the chemical shifts between 7.159 to 9.089 ppm are due to aromatic protons, with the protons close to the carbonyls more deshielded and appearing further downfield than those close to the oxygens. The peaks between 1.317 and 4.805 ppm represent the protons in the aliphatic section of the block copolyester. The peak at 2.153 ppm is due to the three equivalent hydrogens of the methyl group on the aromatic section of the polyester. The same rule governing the protons closer to the carbonyls and oxygens in the aromatic section govern those in the aliphatic segment.

The structure for poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) is the same as the structure of the polymer with the nmr spectrum shown in Table 8, except that in this case the aliphatic segment is cis rather than trans. The multiplets in Table 9 occurring between 7.138 and 9.049 ppm belong to the aromatic protons in different environments. The multiple peaks ranging from 1.251 to 4.776 ppm correspond to the protons in the aliphatic section of the block, except the chemical shift at 2.136

Table 8. Proton NMR Spectrum of Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate) in $CDCl_3$.

ppm	Integral
9.089	4.178
8.517	16.985
8.487	20.802
7.750	6.826
7.720	11.188
7.689	7.812
7.384	4.367
7.351	10.291
7.320	9.037
7.263	4.128
7.189	22.162
7.159	19.359
4.805	4.254
2.881	.990
2.596	3.008
2.233	2.479
2.153	21.890
2.099	8.154
1.768	3.844
1.699	3.681
1.317	7.140

Table 9. Proton NMR Spectrum of Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate) in $CDCl_3$.

ppm	Integral
9.049	2.656
8.499	2.755
8.470	3.404
7.704	1.496
7.335	1.086
7.328	.460
7.304	1.243
7.259	.484
7.170	3.378
7.153	.321
7.138	2.948
4.776	.754
2.636	1.944
2.621	1.042
2.393	.374
2.221	2.550
2.186	1.642
2.152	1.038
2.136	10.119
2.087	7.040
2.027	1.875
1.799	2.790
1.785	1.888
1.776	1.558
1.764	2.249
1.751	2.735
1.708	6.937
1.665	8.680
1.369	11.739
1.336	12.405
1.251	1.245
.000	.450

ppm which belongs to the resonance of the hydrogens of the aromatic methyl group.

The peaks of the proton nuclear magnetic resonance spectra appeared broader than those encountered for low molecular weight compounds. This is not surprising, however, because as the molecular weight of a particular compound increases, the rate of molecular reorientation decreases and therefore, the peaks obtained broaden. The carbon-13 chemical shifts[43] are observed over a range (expressed in ppm) about 20-fold greater than that of protons. The shielding behaviorial pattern of the various groups is seen to be similar for the carbon nuclei and the protons, with aromatic and electronegative groups deshielding more effectively than the aliphatic hydrocarbon side chains. The advantages associated with carbon-13 nmr are firstly, the carbonyls can be observed, and secondly, one can see both the cis and trans products in stable coexistence, which will correspond to a disordered structure as regards the ester linkages. Proton spectra are rather less impressive because of the greater band width of the peaks, which tends to frustrate quantitative interpretation and sometimes makes qualitative interpretation difficult.

Infrared spectroscopy has been used for many years as a tool of elucidating polymer structure.[43,44] This technique was employed in characterizing the synthesized polymers and block copolymers.

In Table 10, the absorptions observed for the polyester block copolymer can be seen to be a combination of the absorptions for the aliphatic and aromatic polyesters.

Table 10. Infrared Absorptions of Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) 1-PEAL-1; Poly(1,4-phenylene terephthalate), 1-PEAL-1, and Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate: 1,4-phenylene terephthalate) 1-PEBL-1 in Potassium Bromide, KBr.

1-PEAL-1 cm^{-1} Energy (λ/ μm)	1-PEAR-1 cm^{-1} Energy (λ/μm)	1-PEBL-1 cm^{-1} Energy (λ/μm)
3420 (2.92)	3430 (2.91)	3420 (2.92)
2940 (3.40)	3070 (3.27)	2940 (3.40)
2860 (3.50)	1730 (5.78)	2860 (3.50)
1720 (5.81)	1600 (6.)	1720 (5.81)
1450 (6.90)	1500 (6.67)	1600 (6.)
	1450 (6.90)	
1370 (7.30)	1410 (7.10)	1500 (6.67)
1330 (7.41)	1250 (8.00)	1450 (6.90)
1250 (8.00)	1160 (8.62)	1410 (7.10)
1165 (8.60)	1070 (9.35)	1370 (7.30)
1040 (9.61)	1010 (9.90)	1320 (7.62)
		1250 (8.00)
		1170 (8.55)
		1080 (9.25)
		1040 (9.61)
		1015 (9.80)

A broad peak appears at 3420 cm^{-1} which is due to the terminal O-H stretching. The strong absorption at 2940 cm^{-1} with a shoulder at 2860 cm^{-1} corresponds to C-H stretching,and the strong peak at 1720 cm^{-1} owes to the stretching of the carbonyls. In the isolated prepolymers, we see that the carbonyl peak for the aliphatic polyester, 1-PEAL-1, is at 1730 cm^{-1} and that for the aromatic polyester, 1-PEAR-1, is at 1720 cm^{-1}. In regular low molecular weight esters, we expect the carbonyl stretch band of the unconjugated ester to lie close to 1740 cm^{-1} and the conjugated carbonyl of the aromatic ester to be shifted to around 1725 cm^{-1}. Fair agreement was obtained. Vibrations peculiar to the aromatic ring are observed at approximately 1600 cm^{-1} (6.25) and 1500 cm^{-1} (6.67) with the later absorption being more intense. The absorption at 1450 cm^{-1} in the aliphatic polyester and in the block is in part caused by a C-H bending and in part by an aromatic ring vibration. The peak at 1370 cm^{-1} is also due to C-H bending. The 1330 cm^{-1} peak is due to O-H deformation in the end group of the aliphatic polyester. The absorption at 1410 cm^{-1} observed in the aromatic polyester and the block are due to aromatic C-H deformation. The several bands between 1250 and 1000 cm^{-1} always accompany the carbonyl stretch. The bands at 1250 cm^{-1} and 1170 cm^{-1}, observed for both the aliphatic and aromatic polyesters and the block copolyester ester, correspond to C-O (-$\overset{O}{\overset{\|}{C}}$O) stretch. The band at 1250 cm^{-1} is stronger than the carbonyl stretch for aromatic polyester and less intense for the aliphatic and block. The absorption at 1080 cm^{-1} is due to the O-C (-O-C-C) stretching. The peak at 1040 cm^{-1} is characteristic of aliphatic esters and polyesters, while that at 1010 cm^{-1} is peculiar to some aromatic polyesters. The aromatic C-H stretching around 3030 cm^{-1} was too weak to be detected.

For Table 11, the assignment and explanation of the absorption bands are almost identical to those given for Table 10. Although prepared separately, 3-PEAL-1 is the same as 1-PEAL-1. Since the polyester block copolyester, 3-PEBL-1, shows absorptions that are a combination of the absorptions for the aliphatic (3-PEAL-1) and the aromatic (3-PEAR-1) polyesters, all explanations will be given using its absorptions. The peak at 3420 cm^{-1} is due to the O-H stretch, while those at 2930 and 2860 cm^{-1} are the C-H stretchings. The carbonyl peak appears at 1720 cm^{-1}, and the absorptions at 1605, 1575 cm^{-1}, which are characteristic of the aromatic ring, appear as a doublet. The absorption at 1460 cm^{-1} represents an aromatic C=C in-plane vibration. The 1365 cm^{-1} absorption is due to C-H bending, while the 1400 cm^{-1} band is due to the C-H deformation. The strong bands between 1080 and 1250 cm^{-1} correspond to the -C-O-C- stretches. The peak at 1035 cm^{-1} is characteristic of aliphatic polyesters and that at 1010 cm^{-1} is typical of aromatic polyesters. The weak absorption at 3060 cm^{-1} in the aromatic prepolymer, 3-PEAR-1, is due to aromatic C-H stretching, while the weak bands at 2920 and 2840 cm^{-1} are due to the stretching of the methyl group on the aromatic prepolymer. These bands are, of course, embedded in the absorptions of the methylene C-H stretching observed for the block, 3-PEBL-1. The bands considered to be of most help in diagnosing the aromatic character of the polymers appear in the region between 1650 and 1400 cm^{-1}. There are normally four bands in this region, at about 1600, 1585, 1500, and 1450 cm^{-1}, which are due to the C=C in-plane vibrations.

In Table 12, the broad absorptions at 3420 cm^{-1} (in the block copolyester) and 3445 cm^{1} (in the aromatic polyester) are due to O-H stretching. The O-H stretch is carboxylic O-H in the case of 4-PEAR-2. The weak band at 3060 cm^{-1} corresponds

Table 11. Infrared Absorptions of Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate), 3-PEAL-1; Poly(2-methyl-1,3-phenylene terephthalate), 3-PEAR-1; and Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate : 2-methyl-1,3-phenylene terephthalate), 3-PEBL-1, in KBr.

3-PEAL-1 Energy/cm^{-1} (λ/μm)	3-PEAR-1 Energy/cm^{-1} (λ/μm)	3-PEBL-1 Energy/cm^{-1} (λ/μm)
3420 (2.92)	3420 (2.92)	3420 (2.92)
		3060 (3.27)
2940 (3.40	3060 (3.27)	2930 (3.40)
2860 (3.50)	2920 (3.42)	2860 (3.50)
1720 (5.81)	2840 (3.51)	1720 (5.81)
1450 (6.90)	1730 (5.78)	1605 (6.25)
1370 (7.30)	1610 (6.21)	1575 (6.35)
	1575 (6.35)	1460 (6.85)
1250 (8.00)	1460 (6.85)	1400 (7.15)
1165 (8.60)	1400 (7.15)	1365 (7.33)
1040 (9.61)	1255 (7.97)	
	1220 (8.20)	1245 (8.03)
	1180 (8.48)	1220 (8.20)
	1155 (8.65)	1155 (8.65)
	1080 (9.25)	1080 (9.25)
	1010 (9.90)	1035 (9.7)

Table 12. Infrared Absorptions of Poly(trans-1,2-cyclohexalane-trans-cyclohexane-1,2-dicarboxylate), 4-PEAR-2; Poly(2-methyl-1,3-phenylene isophthalate), 4-PEAR-2; and Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate), 4-PEBL-2 in KBr.

4-PEAL-2 cm^{-1} Energy/cm^{-1} (λ / μm)	4-PEAR-2 cm^{-1} Energy/cm^{-1} (λ / μm)	4-PEBL-2 cm^{-1} Energy/cm^{-1} (λ / μm)
3420 (2.93)	3440 (2.91)	3420 (2.92)
2930 (3.40)	3060 (3.27)	3060 (3.27)
2860 (3.50)	2920 (3.44)	2965 (3.37)
1725 (5.80)	2850 (3.47)	2850 (3.47)
1445 (6.92)	1735 (5.76)	1730 (5.78)
	1600 (6.25)	1600 (6.25)
1250 (8.00)	1580 (6.33)	1580 (6.33)
1170 (8.55)	1460 (6.85)	1460 (6.85)
1110 (9.00)	1430 (7.00)	1290 (7.73)
1035 (9.70)	1375 (7.33)	1200 (8.33)
	1295 (7.72)	1160 (8.62)
	1200 (8.33)	1080 (9.27)
	1155 (8.65)	1065 (9.38)
	1085 (9.25)	1035 (9.70)
	1065 (9.38)	1000 (10.00)
	1000 (10.00)	

to the C-H stretching, while the absorptions at 2965 and 2850 cm^{-1} represent the aliphatic C-H stretching in the block copolyester. The C-H stretch for the methyl group in the aromatic prepolymer was displayed at 2920 and 2850 cm^{-1}. The 1730 cm^{1} band is the carbonyl stretch and the absorptions at 1600 and 1580 cm^{-1}, which appear as a doublet, are typical of an aromatic ring. The bands between 1290 and 1160 cm^{-1} correspond to the -C-O stretch, and the absorption at 1080 cm^{-1} with a shoulder at 1065 cm^{-1} stems from the O-C stretch. The 1035 cm^{-1} absorption is typical of aliphatic polyesters and that around 1000 cm^{-1} is characteristic of aromatic polyesters. These two bands are observed in the block copolyester. The above absorptions can be seen to be a combination of the aliphatic and aromatic polyester absorptions.

In Table 13, the 3400 cm^{-1} absorption is the O-H stretching. The peak at 3060 cm^{-1} (5-PEAR-1) corresponds to aromatic C-H stretch, and the bands at 2920 and 2850 cm^{-1} in the block copolyester, represent the methylene C-H stretching from the aliphatic polyester and the methyl C-H stretch from the aromatic polyester. The strong carbonyl peak at 1720 cm^{-1} is accompanied by absorption bands ranging from 1075 to 1280 cm^{-1} due to the -C-O-C stretch. The doublet at 1600 and 1575 cm^{-1} represents the absorptions of the aromatic nucleus.

From Table 14, we wee that the absorptions of the polyamide block copolymer are a combination of the absorptions of the individual aromatic and aliphatic polyamides. The broad 3320 cm^{-1} absorption is due to the secondary amide N-H stretching vibrations. In the aliphatic (2-PAAL-1) polyamide this vibration occurred at 3300 cm^{-1}. This absorption is characteristic of secondary amides which are highly hydrogen bonded, and in which the carbonyl group and the

Table 13. Infrared Absorptions for Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate), 5-PEAL-1; Poly(2-methyl-1,3-phenylene isophthalate), 5-PEAR-1; and Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate : 2-methyl-1,3-phenylene isophthalate), 5-PEBL-1 in KBr.

5-PEAL-1 Energy/cm^{-1} (λ/ μm)	5-PEAR-1 Energy/cm^{-1} (λ / μm)	5-PEBL-1 Energy/cm^{-1} (λ / μm)
3400 (2.94)	3400 (2.94)	3400 (2.94)
2920 (3.44)	3060 (3.27)	2920 (3.44)
2850 (3.47)	2920 (3.44)	2850 (3.47)
1720 (5.81)	2850 (3.47)	1720 (5.81)
1440 (7.95)	1730 (5.78)	1600 (6.25)
1300 (7.70)	1590 (6.29)	1575 (6.35)
1250 (8.00)	1580 (6.37)	1440 (7.95)
1170 (8.55)	1460 (6.85)	1280 (7.81)
1110 (9.00)	1430 (7.00)	1200 (8.33)
1030 (9.70)	1295 (7.72)	1160 (8.62)
	1200 (8.33)	1075 (9.30)
	1150 (8.70)	1030 (9.70)
	1085 (9.25)	
	1060 (9.43)	

Table 14. Infrared Absorptions for Poly(1,2-cyclohexalene-trans-cyclohexane-1,4-dicarboxamide), 2-PAAL-1; Poly(1,4-phenylene terephthalamide), 2-PAAR-1; and Poly(1,2-cyclohexalene-trans-cyclohexane-1,4-dicarboxamide : 1,4-phenylene terephthalamide), 2-PABL-1 in KBr.

2-PAAL-1 Energy/cm^{-1} (λ / μm)	2-PAAR-1 Energy/cm^{-1} (λ / μm)	2-PABL-1 Energy/cm^{-1} (λ / μm)
3300 (3.03)	3320 (3.01)	3320 (3.01)
3070 (3.20)	1640 (6.10)	3060 (3.28)
	1535 (6.35)	
2930 (3.40)	1505 (6.62)	2920 (3.44)
2860 (3.50)	1400 (7.15)	2850 (3.47)
1635 (6.12)	1310 (7.60)	1640 (6.10)
1525 (6.57)	1250 (8.00)	1540 (6.45)
1250 (8.00)	1105 (9.09)	1500 (6.67)
1200 (8.33)	1013 (9.90)	1400 (7.15)
		1300 (7.70)
		1250 (8.00)
		1100 (9.09)
		1013 (9.90)

N-H group are trans to each other. This vibration (3300 cm^{-1} for 2-PAAL-1) confirms that the product, poly(1,2-cyclohexalene-trans-cyclohexane-1,4-dicarboxamide) has its carbonyl and N-H groups in the trans-position as expected. This is also seen to be retained in the block copolyamide. The weak band at 3070 cm^{-1} is characteristic of secondary amides and polyamides; but this cannot distinguish between a cis and a trans product because both products display this weak band. The strong peaks at 2920 and 2850 cm^{-1} observed in the block (2-PABL-1) and the aliphatic (2-PAAL-1) polymers are due to the C-H stretching vibrations of the methylene groups. A strong absorption at 1640 cm^{-1} is observed for the polyamides and block copolyamides. This is called the amide I band and is due to the carbonyl stretching. At 1540 cm^{-1} is the amide II band which represents the N-H (-C-N-) stretching. The band at 1400 cm^{-1} is just due to an aromatic C-H deformation. The amide III bands at 1300 and 1250 cm^{-1} are due to the CN stretching and N-H deformation respectively. The bands at 1100 and 1013 cm^{-1} are merely due to C-H deformation of the 1,4-disubstituted benzene rings.

Examination of the infrared data for the polyesters, polyamides, block copolyesters, and polyamide block copolymer reveals that the absorptions observed for polyesters and polyamides do not vary significantly from those observed for low molecular weight esters and amides.

Solubility of the polymers is a prerequisite for most physical measurements. Some of the polymers and block copolymers are insoluble in most organic solvents. The poly(1,4-phenylene terephthalate) is highly insoluble because of its high degree of crystallinity, and the poly(1,4-phenylene terephthalamide) is only soluble in

concentrated sulfuric acid. The characteristic insolubility behavior displayed by some of these macromolecules made measurement of viscosities and determination of molecular weights impossible.

Generally, viscosity is a measure of the ability of a polymeric material to retard the flow rate of a solvent and is found to be dependent on molecular weight. Polymers with higher viscosities, in general have higher molecular weights. In making viscosity measurements, the polymer solutions are not allowed to stand for many days before measurements are made since the solutions may otherwise become culture media for airborne bacteria.[45]

There are four types of viscosities[46,47] that can be determined through measurements of relative viscosity. These are specific, reduced specific, inherent, and intrinsic viscosities. Relative viscosity is defined as:

$$\eta_{rel} = t/t_o \qquad (3)$$

where t_o is the flow time through a viscometer of a reference liquid (solvent) and t is the flow time through the same viscometer of the dilute solution of polymer in the reference liquid. The inherent viscosity is defined as:

$$\eta_{inh} = \ln(\eta_{rel})/C \qquad (4)$$

where c is the concentration of the polymer solution in g/100 ml of solvent. Results are therefore reported in deciliters per gram (dL/g).

Viscosity and elemental analysis are used as methods for characterizing polymers. Elemental analysis for the homopolymers or prepolymers are closer to theoretical values than those for the block copolymers due to the fact that block

Table 15. Elemental Analysis and Viscosity Data for Polyesters, Polyamides, Block Copolyesters and Block Copolyamide.

Polymers	C	H	N	C	H	N	η_{inh}
Poly(1,4-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) 1-PEAL-1	65.31	8.11		65.30	7.82		
Poly(1,4-phenylene terephthalate) 1-PEAR-1	68.53	3.44		68.52	3.67		
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate: 1,4-phenylene terephthalate) 1-PEBL-1	67.89	5.31		67.07	6.51		
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate) 3-PEAL-1	66.54	8.00		66.53	8.03		0.25
Poly(2-methyl-1,3-phenylene terephthalate) 3-PEAR-1	70.78	4.00		69.68	3.95		
Poly(1,4-cyclohexalene-trans-cyclohexane-1,4-dicarboxylate: 2-methyl-1,3-phenylene terephthalate) 3-PEBL-1	68.74	5.90		68.57	6.01		
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) 4-PEAL-1	64.90	8.17		64.74	7.91		0.11
Poly(2-methyl-1,3-phenyl isophthalate) 4-PEAR-1	69.18	4.47		68.99	7.03		0.13

Table 15 (Continued).

Polymers	C	H	N	C	H	N	η_{inh}
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 4-PEBL-1	66.97	6.03		66.44	7.03		0.20
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate) 4-PEAL-2	65.13	8.14		65.11	7.95		0.16
Poly(2-methyl-1,3-phenylene isophthalate) 4-PEAR-2	69.36	3.89		69.31	3.81		0.20
Poly(trans-1,2-cyclohexalene-trans-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 4-PEBL-2	68.29	5.94		68.05	5.75		0.26
Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate) 5-PEAL-1	62.88	7.64		62.28	7.63		0.06
Poly(2-methyl-1,3-phenylene isophthalate) 5-PEAR-1	68.53	3.88		68.41	4.01		0.21
Poly(cis-1,2-cyclohexalene-cis-cyclohexane-1,2-dicarboxylate: 2-methyl-1,3-phenylene isophthalate) 5-PEBL-1	66.90	6.23		66.35	6.01		0.25
Poly(1,2-cyclohexalane-trans-cyclohexane-1,4-dicarboxyamide) 2-PAAL-1	65.17	8.79	10.86	65.01	9.14	10.66	0.25 (98% H_2SO_4)

Table 15 (Continued).

Polymers	C	H	N	C	H	N	η_{inh}
Poly(1,4-phenylene terephthalamide) 2-PAAR-1	68.37	4.27	10.64	68.17	4.46	10.96	0.41 (98% H_2SO_4)
Poly(1,2-cyclohexalene-trans-cyclohexane-1, 4-dicarboxamide: 1,4-phenylene terephthalamide) 2-PABL-1	67.76	6.68	10.93	67.08	6.25	10.87	0.46 (98 % H_2SO_4)

copolymers are rarely free of homopolymer impurities. Values of elemental analysis and viscosities are given in Table 15.

The elemental analysis for 1-PEAL-1, 1-PEBL-1, 2-PAAL-1, 2-PAAR-1, 2-PABL-1, 3-PEAR-1 do not correspond with the theoretical results when calculated with the appropriate end groups. This is due to the degradation of the polymers by the potassium hydroxide and hydrochloric acid solutions used in washing the polymers. Ester and amide interchanges[48] are observed in the presence of alkali and acids. The bonds between the nitrogen atom and the carboxylic carbon, and those between the oxygen and the carboxylic carbon $(H\bar{N} - \overset{O}{\overset{\|}{C}}, \quad \bar{O} - \overset{O}{\overset{\|}{C}}+)$ are polar owing to the polarizing effect of the oxygen atom of the carbonyl. The polar nature of these bonds therefore causes the linkages to have very low resistances to acids and alkalides. As a result of these ester and amide interchanges, the polyamides and polyesters are degraded in the presence of some strong acids and bases. It may be due to this degradation that we also obtained low inherent viscosity measurements. The 3-PEAL-1, which is the same as 1-PEAL-1, was washed with only water, acetone, and alcohol. This gave better results for the elemental analysis. The polyesters (especially the aromatic polyesters with 1,4-disubstitutions) formed a very dark solution on treatment with dilute sodium hydroxide solution. Observation of coloration in polymers[49] is usually a sign that degradation has taken place.

Conclusion

The polymers and block copolymers synthesized were confirmed by the characterization methods to be polyamides, polyesters, block copolyamide, and block copolyesters. It is also found that these polymers and block copolymers are high-melting. This makes their use as fiber materials possible. It is also found that none of the characterization methods can, by itself, adequately confirm the structures of the polymers. For example, the n.m.r. data cannot, by itself, show that the products were polyamides and polyesters, therefore, the infrared was used concertedly. The viscosity numbers and elemental analysis gave a general idea of the degrees of polymerization.

The properties associated with these polymers and block copolymers suggest that they have good fiber properties. The block copolymers have additive properties of their corresponding prepolymers.

Products of widely different characteristics may be obtained depending upon reactants and the degree of polymerization. This is generally typical of polymers. Some of the properties of a polymer depend upon the molecular weight of the polymer and the monomers employed in polymerization. Some of the linear polyesters and polyamides are crystalline and this crystallinity may be altered by introducing meta- or ortho- reactants.

As has been previously stated, the general techniques and conditions employed in this research follow known practices in the field of polymer chemistry. Even though certain representative polymers have been prepared and characterized in order to illustrate this technique, it will be obvious to those skilled in this art that various changes and modifications may be made therein without deviating from the spirit or scope of this research.

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